

# KINETICS OF THE FORMATION OF INTERCALATION COMPOUNDS IN CRYSTALLINE GRAPHITE

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## 1 ABSTRACT

Crystalline graphite is known to form intercalation compounds with bromine and nitric acid. Their formation was studied using thermal measurements and analytical techniques. Samples of graphite treated with either bromine or nitric acid were prepared by contacting these reagents at room temperature with powdered crystalline graphite. The bromine treated graphite showed a greater evidence of the formation of an intercalation compound. Samples of bromine treated graphite were analyzed utilizing X-Ray Diffraction, Thermogravimetric Analysis, and Differential Scanning Calorimetry, DSC. The formation of a distinct intercalation compound at lower temperatures was observed. At higher temperatures, the intercalation compound decomposed to yield the additive species in a state of mobility constrained to two dimensions. Kinetics of the formation of the intercalation compound with bromine were analyzed.

## 2 INTRODUCTION

Crystalline graphite has a structure that can be best described as an ordered stack of flat aromatic layers. A typical structural representation of graphite is shown in Figure 1. The bonds between carbon atoms in the same layer are strong giving the layers a powerful internal cohesion. But there is little cohesion between successive layers which experience only weak Van der Waal's forces. The highly anisotropic nature of such a structure imparts to graphite certain important physical and chemical properties. One result of this anisotropy is that certain compounds (e.g., halogens, alkali metals, oxy-acids) can be inserted<sup>1</sup> between different layers of the graphite structure. The inserted reagents often occupy symmetrical positions with respect to the carbon atoms which are themselves in hexagonal arrangements in each layer. Two possible geometrical representations of the inserted species in relation to the carbon layers are shown in Figure 2. The inserted reagents are believed to be partly ionized, i.e. the carbon layers either give or receive electrons. Therefore, two types of reagents can be distinguished according to whether the inserted species is positively charged (e.g. alkali metals) or negatively charged (e.g. some halogens and oxy-acids) with respect to the carbon layers.

Depending on the temperature, the inserted substance may form a weak (intercalation) compound with graphite or it may move freely between layers in a

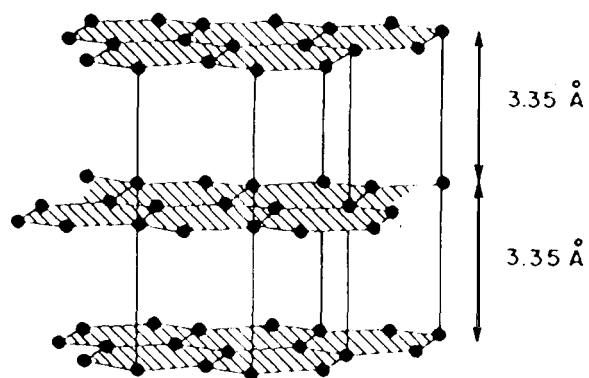


Figure 1 The structure of graphite

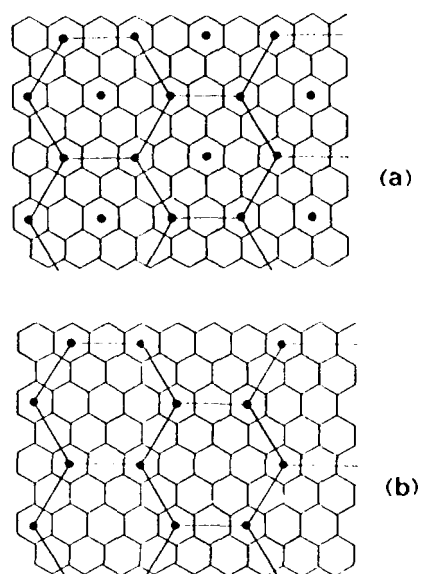


Figure 2 Two possible representations of the inserted species in relation to the carbon layers

strictly two-dimensional manner. Most intercalations are accompanied by a macroscopic swelling and large changes in surface and bulk properties such as color, luster, electrical conductivity, and magnetic properties. For example, the sulfuric acid compound looks steel blue, and the alkali-metal compounds have a copper tint. A special feature of a certain of these compounds is the appearance of a metallic sheen. The swelling is easily explained by the fact that the layer must move apart to make room for the reagent layers, and this is confirmed by X-ray diffraction. The metallic aspect of the compounds seems to indicate a significant change in the electronic structure of the graphite. This is confirmed by the change in the electronic properties after insertion. For example, the electrical conductivity is 10 to 20 times higher in these compounds than in graphite.

The intercalation and decomposition processes are characterized by the intercalation isotherms which show a pressure dependence of the extent of intercalation. Also common is the existence of a residue compound which refers to residual intercalation even when the pressure is reduced to zero. It is also known that intercalation occurs by whole layers at a time. Further, the inserted species under some conditions may behave as a two dimensional fluid.

A two-dimensional fluid is defined as one where its mobility is restricted to two dimensions or to a surface. Consequently, its mobility is influenced by the surface interactions. While two-dimensional fluids have not received a lot of attention, some previous work in this area has been carried out by Gland<sup>2</sup>, Toxvaerd<sup>3</sup>, and Nixon et al<sup>4</sup>. Some interesting systems are found due to formation of intercalation compounds in graphite as described by Hooley<sup>5</sup> and Robert et al.

The intercalation of graphite was carried out with both bromine and nitric acid. With the experimental procedure used, the intercalation of graphite with nitric acid did not take place to a significant extent to allow an investigation of the kinetics of the process. However, the kinetics of intercalation of bromine in graphite layers was studied utilizing analytical techniques. Samples of bromine-treated graphite were prepared by contacting bromine vapor at room temperature with powdered crystalline graphite. Untreated and bromine-treated samples were analyzed by (1) X-Ray Diffraction at various temperatures, and (2) Differential Scanning Calorimetry, DSC. Mobility parameters were inferred from the above data.

### 3 EXPERIMENTAL

The exposure of graphite to bromine (or nitric acid) was carried out at room temperature in a glass apparatus which consists of two flasks connected together by a stop cock. This configuration is shown in Figure 3. One of these flasks contains a quartz basket with a porous frit which contains the graphite sample. The second flask contains liquid bromine (or nitric acid) at room temperature.

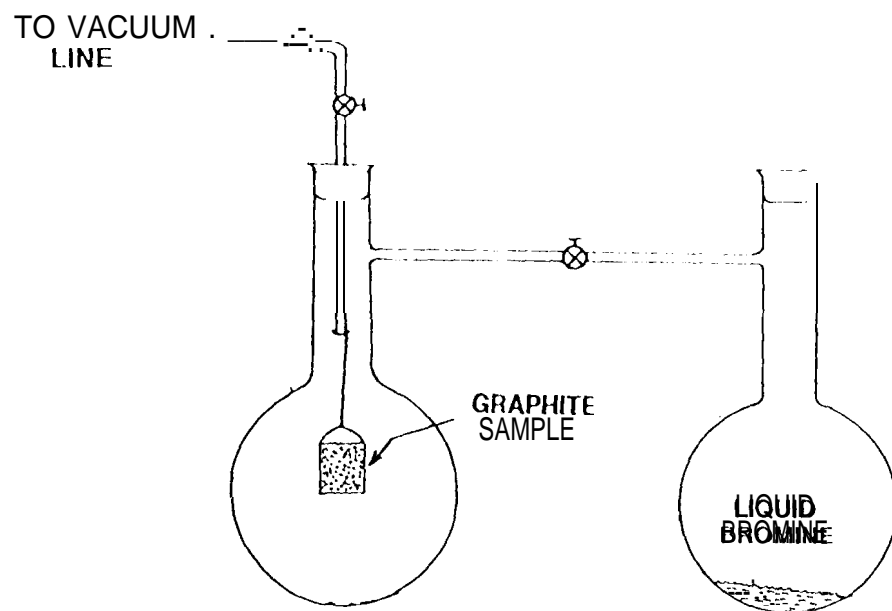


Figure 3 Schematics of the apparatus used for intercalating graphite with bromine

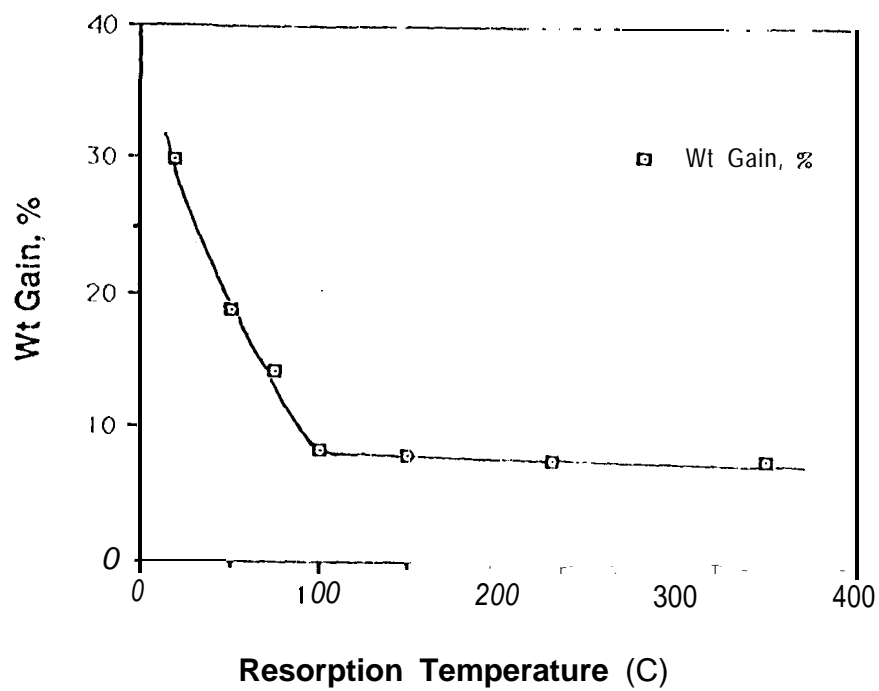


Figure 4 Effect of temperature on bromine staying with the treated graphite

Initially, the flask with the graphite sample is evacuated to desorb the graphite. Then the stop cock between the two flasks is opened to let the bromine (or nitric acid) vapor in this flask. The vacuum is gradually applied to purge the flask of all air. After 5 minutes of evacuation at 24 inch-Hg vacuum, the vacuum line is cut off and the two flasks are allowed to equilibrate at room temperature. The graphite is then allowed to be in contact with bromine (or nitric acid) vapor at room temperature for 48 hrs. At the end of this time, the flask is gradually evacuated again at room temperature for 24 hrs. The quartz holder with the graphite sample is taken out and weighed to determine the bromine (or nitric acid) uptake at room temperature. The quartz holder is then placed back in the flask and insulation is wrapped around the flask. The assembly with the sample holder flask is heated to a temperature of 50 °C for a period of 24 hrs. The flask assembly is then cooled back to room temperature, the quartz sample holder taken out, and weighed again. This procedure is repeated by successively desorbing the graphite sample at temperatures of 100, 150, 200, 250 and 350 °C. These measurements result in a quantitative tabulation of the bromine uptake capacity by the graphite at different temperatures.

### 3.1 Sample Analysis: by X-ray Diffraction

A Siemens D500 Diffractometer with KAVEX energy dispersive X-ray detector was used for XRD analysis. A rectangular stainless steel strip was cut and placed over the platinum strip used to support the sample for XRD analysis. The sample to be analyzed was placed in the middle of the stainless steel strip and held in place by bending the edges of the strip forming a lip. This special sample placement was carried out to accommodate the heating of the highly reactive samples being handled in these tests. The radiation used in scanning the X-ray spectrum had a wavelength corresponding to  $\text{CuK}\alpha$ . No response in the close range of investigation was seen from the stainless steel. Therefore, the spectrum was attributed to the bromine containing graphite sample.

Each prepared material and an unexposed baseline control sample were analyzed using a DuPont 951 Thermogravimetric Analyzer (TGA) and a DuPont 910 Differential Scanning Calorimeter (DSC). The samples were heated at 10 °C/min to 600 °C under flowing argon at 100 cm<sup>3</sup>/min. From the TGA, the resorption of the bromine was determined as a function of temperature. The effect on heat capacity of the intercalated bromine was determined by DSC. The outgassing products of the treated samples were characterized independently using a Hiden quadrupole mass spectrometer. The mass spectroscopy was conducted with the samples placed in a heated quartz sample holder, with the outgassed products entering the vacuum side of the mass spectrometer through a needle valve. The samples were heated at approximately 5 °C/min to 400 °C. The outgassed composition was scanned at  $m/e$  ratios of up to 200 atomic mass units, with particular emphasis on the mass spectra at 79.9 for bromine and 63 for nitric acid.

## 4 RESULTS AND DISCUSSION

### 4.1 Bromine Treated Samples

For the bromine treated graphite sample, the sample weight gain due to bromine uptake as a function of the resorption temperature is shown in Fig. 4. It is seen that the weight gain approaches a residual value of about 8 percent at a resorption temperature of about 150 °C.

The mass spectrometer analysis of the sample having undergone desorptions up to 350 °C showed that no bromine came out of the sample during heating under high vacuum up to 450 °C. This shows that the residual bromine in the sample is in some type of a bond with the carbon.

The XRD scans for the plain (as received) and treated graphite samples are shown in Figures 5 and 6. Figure 5 shows the signal intensity vs.  $2\theta$  for a regular scan. Figure 6 shows a similar but slower scan with increased signal averaging time. It is seen that there is a distinct peak at  $2\theta = 20.8$  degrees for the bromine treated sample which is absent for the plain sample. This was the only significant difference between the plain and the treated samples.

The bromine treated sample was gradually heated from room temperature to 300 °C and the X-ray diffraction scans were taken at 50 °C intervals. These scans are shown in Fig. 7. It was seen that the aforementioned peak at  $2\theta = 20.8$  decreased with increasing temperature and was practically non existent at 300 °C. However, when the sample was allowed to cool back to room temperature, this peak reappeared at the original intensity. This effect may be directly inferred from Figure 8 which compares the original room temperature peak and the later one obtained after cooling the sample.

The TGA plots for the untreated and the bromine treated samples (with the residual compound) are shown in Figure 9. The treated sample loses its mass with the increase of temperature at a rate slightly higher than the untreated sample. The DSC plots for the untreated and the bromine treated samples are shown in Figure 10. From these plots, heat capacities as a function of temperature can be obtained and are plotted in Figure 11. It is seen that the heat capacity for the treated sample is significantly higher than the corresponding heat capacity for the untreated sample. This is in agreement with the expectation that a fraction of the total heat capacity is associated with bromine (and its possible mobility) for the bromine treated sample.

### 4.2 Nitric Acid Treated Samples

The uptake of nitric acid after subjecting the treated sample to a vacuum at room temperature was only about 2 percent. As this uptake was below the threshold value to see any possible effect in the XRD spectra, the XRD analysis was not carried out. However, the resorption from the treated sample was

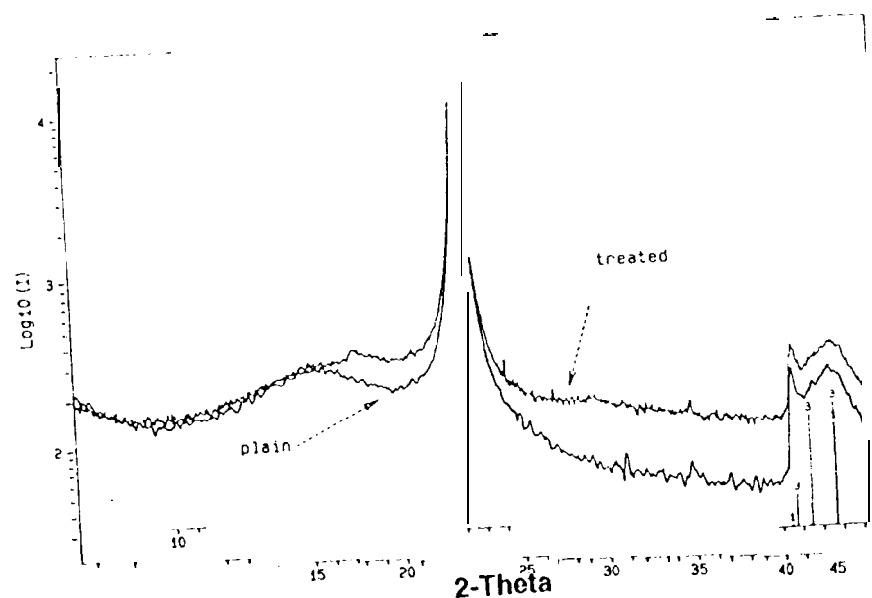


Figure 5 X-ray diffraction spectra of plain and bromine treated graphite in normal scans

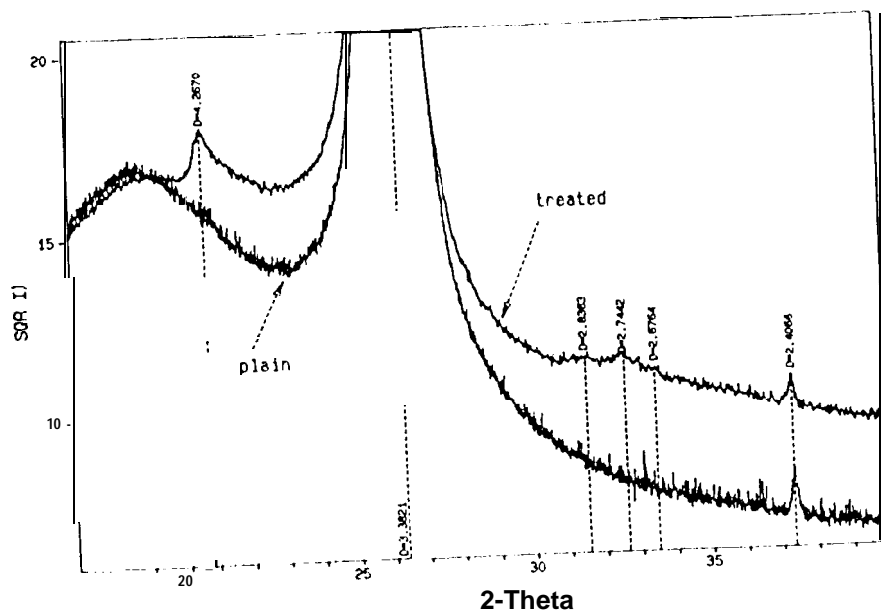


Figure 6 X-ray diffraction spectra of plain and bromine treated graphite in "o" scans on an expanded 2-theta scale

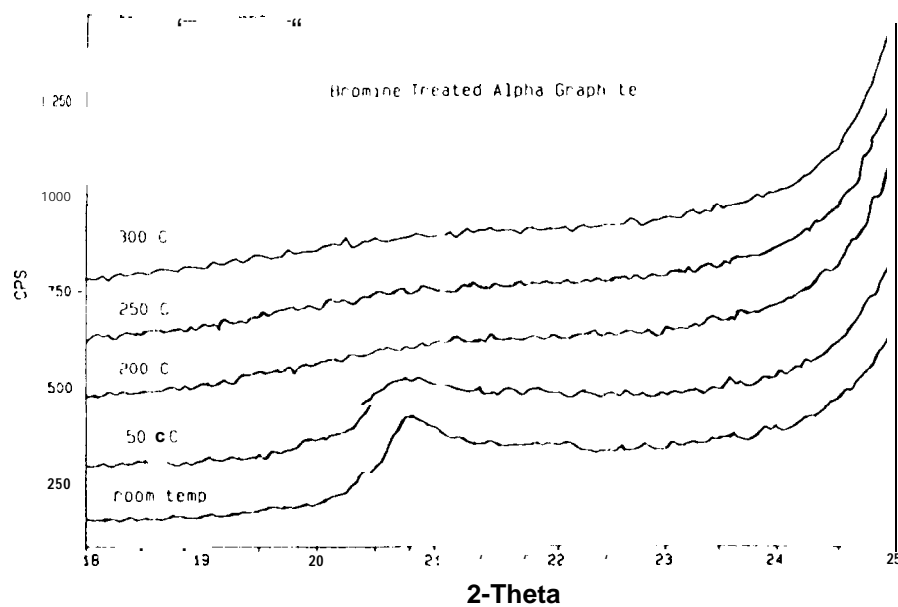


Figure 7 Temperature dependence of the X-ray diffraction spectra for the graphite sample with residual intercalated bromine

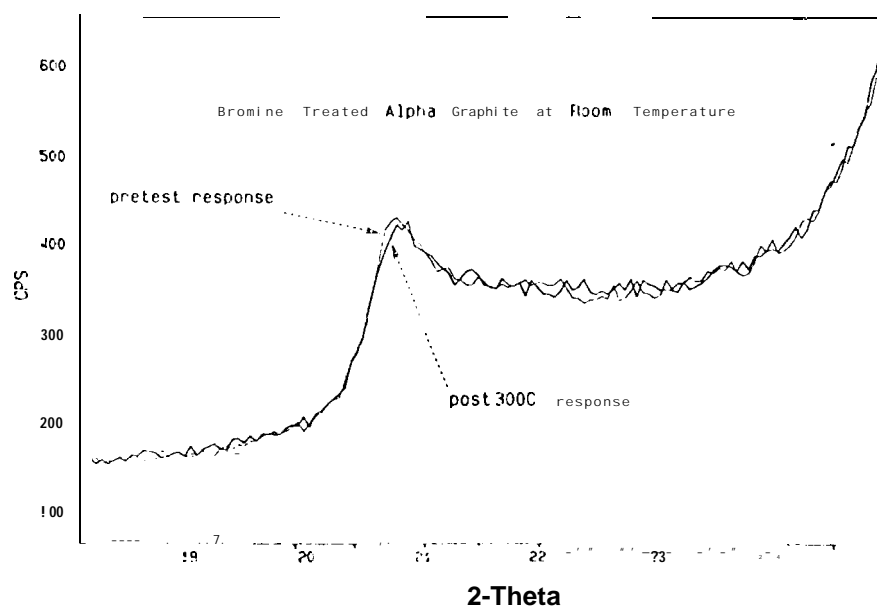


Figure 8 A room temperature comparison of the X-ray diffraction spectra for the graphite sample with residual bromine before and after subjecting it to 300 °C heating cycle



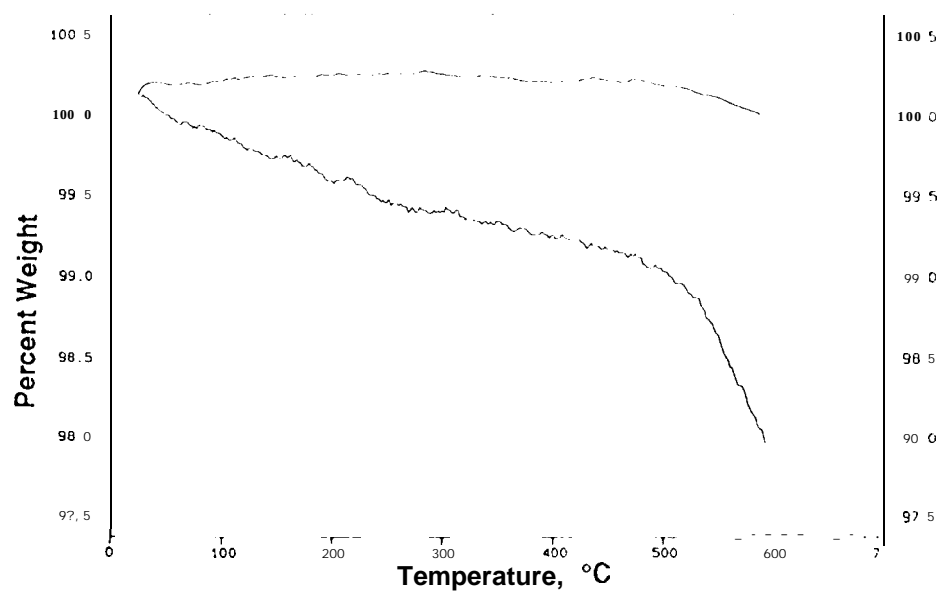


Figure 9 Sample weight change as a function of temperature from the thermogravimetric analyzer for the plain and the bromine treated graphite

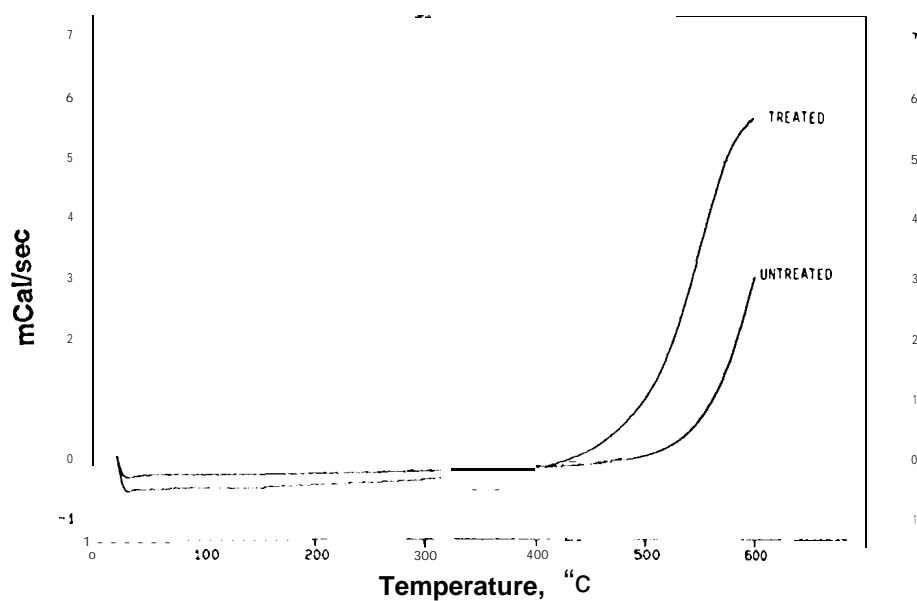


Figure 10 DSC plots for the plain and the bromine treated graphite

studied by gradually heating the sample from room temperature to 400 °C. No  $\text{HNO}_3$  or its fragments evolved from the sample during this heat up period. This suggests that the nitric acid that was taken up may have formed an intercalation compound.

### 4.3 Mobility Parameters

It is possible to derive the mobility parameters from the data on variation in the height of the peak in the XRD spectra corresponding to the intercalated product,  $\text{C}_x\text{Br}$ , with temperature. At lower temperatures, the bromine molecules do not have enough energy to leave the active site on carbon that they are bound to. As the temperature increases, bromine molecules have greater energy and some of them can leave the active site and become mobile. This will cause the observed decrease in the peak height of the intercalated compound in the XRD spectra. It was assumed that the inserted bromine will have no mobility at its melting point of -7 °C. The corresponding signal intensity in the XRD spectrum,  $I_0$ , was obtained by extrapolation of the data to this temperature. At a sufficiently high temperature (e.g. 300 °C), most of the bromine molecules appear to be mobile, and hence, no peak corresponding to the intercalated compound is visible in the XRD spectra. The variation of the normalized signal intensity ( $I/I_0$ , based upon peak heights) with temperature is shown in Figure 12.

Let  $dN$  be the number of molecules having energy between  $\epsilon$  and  $\epsilon + d\epsilon$ . Then, from the Maxwell Boltzmann's distribution of energy for the two dimensional mobility,

$$dN/N = e^{-\epsilon/kT} d\epsilon/kT$$

Let  $\epsilon^*$  be the energy a bromine molecule needs to leave the carbon active site. Let  $f^*$  be the fraction of molecules having energy in excess of  $\epsilon^*$ . Then  $f^*$  is given by

$$\begin{aligned} f^* &= \frac{1}{kT} \int_{\epsilon^*}^{\infty} e^{-\epsilon/kT} d\epsilon \\ &= e^{-\epsilon^*/kT} \end{aligned}$$

or, one may write

$$\ln f^* = -\epsilon^*/kT$$

A plot based upon the above relationship is shown in Fig. 13. It is seen that a straight line may be drawn through most of the data points with the exception of those in the high temperature range. The error associated with the points in the high temperature range is large due to small peak heights. The

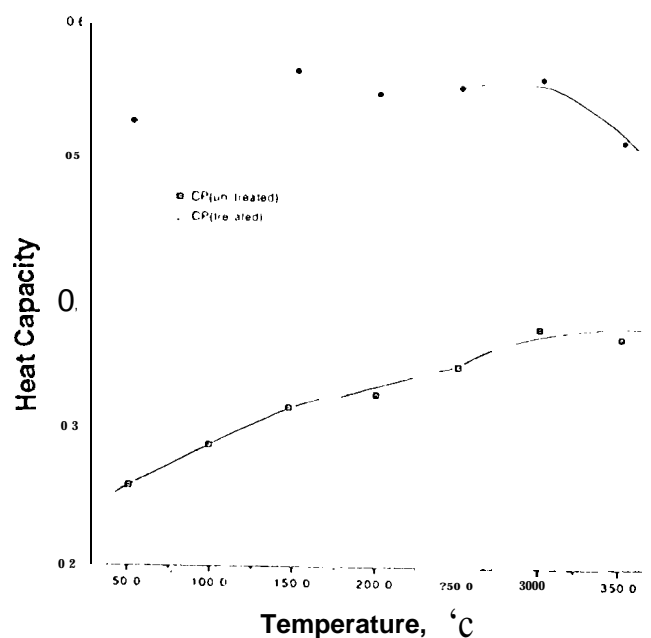


Figure 11 Heat capacities for the plain and the bromine treated graphite deduced from the DSC plots

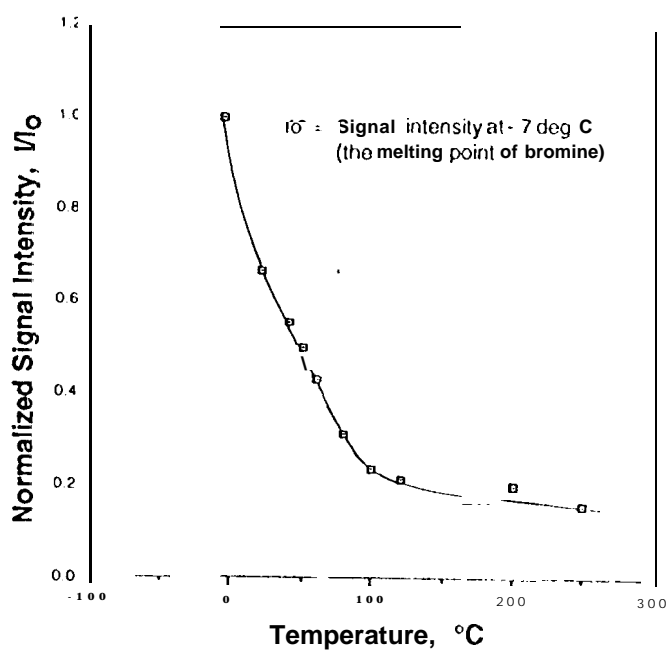


Figure 12 Normalized signal intensity for the intercalated compound (from the XRD spectra) as a function of temperature

slope of the straight line yields a value for the activation energy for mobility of the bromine molecules as 2.03 kcals/g-mole.

## 5 CONCLUSIONS

A strong evidence was seen for formation of an intercalation compound in graphite-bromine interaction at room temperature. Upon increasing the temperature to 300 °C, the intercalation compound is lost. But the bromine is still inside the graphite layers, apparently in a mobile state. The activation energy relating to the transformation of bromine in the mobile state is 2.03 kcals/g-mole.

## 6 ACKNOWLEDGMENTS

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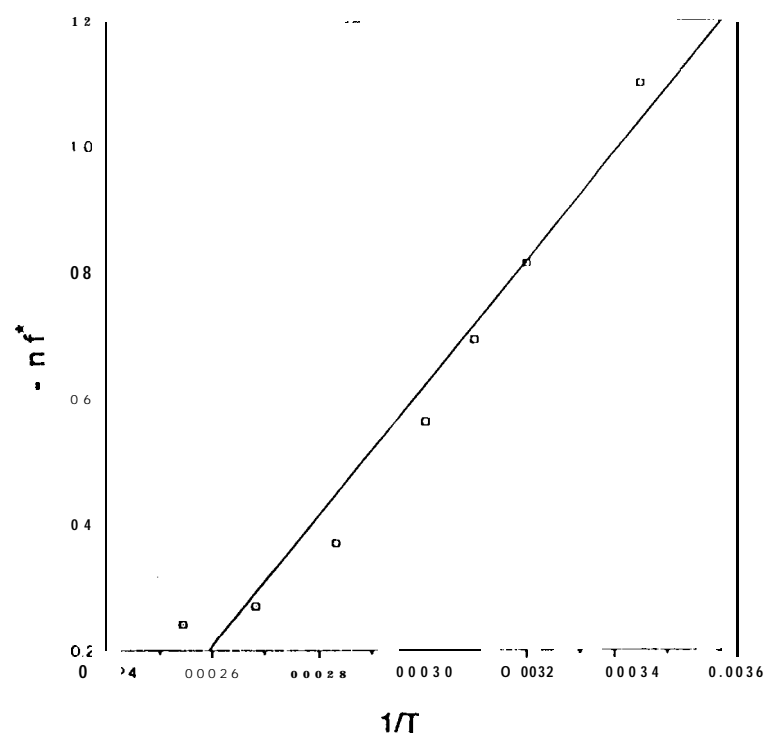


Figure 13 Arrhenius rate dependence of the thermal decomposition of the intercalation compound.